



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> PHOTOCATALYST FOR METHANE CONVERSION, METHOD FOR PREPARING THE SAME AND METHOD FOR PREPARING LOW CARBOHYDRATES USING THE SAME  <b>(57) Abstract</b>  A photocatalyst comprising the composition represented by the Formula (III): M(A)/T, can convert methane into low carbohydrates at high efficiencies without causing the production of pollution of the environment. In said formula, M stands for a metal selected from the group consisting of Pd, Ir, Ru, Cd, Ag and Pt; T stands for a support selected from the group consisting of ZnS (Zn:S 1:1 molar ratio), CdS (Cd:S 1:1 molar ratio) and TiO <sub>2</sub> ; and A represents the amount of the M impregnated, ranging from 0.50 to 3.50 weight % based on the total weight of the photocatalyst (M+A). A metal salt which comprises a catalytically active metal is dissolved in water and mixed with a dried support, in such a way that the metal is present at an amount of 0.50-3.50 weight % based on the total weight of the metal and the support, and the suspension is homogeneously mixed, completely dried, and sintered, to prepare the photocatalyst. Illumination of artificial light upon a homogeneous suspension of the photocatalyst and methane in water can generate low carbohydrates, such as ethane, ethylene and propane, without difficulty at 5-55 °C under a pressure of a vacuum to 5 atm.		

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PHOTOCATALYST FOR METHANE CONVERSION, METHOD FOR  
PREPARING THE SAME AND METHOD FOR PREPARING LOW CARBOHYDRATES  
USING THE SAME

5                   **Technical Field**

The present invention relates, in general, to a novel photocatalyst for methane conversion reaction and, more particularly, to a photoreaction in which low carbohydrates,  
10 such as ethylene, ethane and propane, can be efficiently and economically prepared from methane in the presence of a photocatalyst. Also, the present invention is concerned with a method for preparing the photocatalyst and with a method for preparing low carbohydrates using the photocatalyst.

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**Background Art**

For longer than one hundred years, petroleum has been a peerless major energy source. Although continuing to be used  
20 for this purpose, petroleum has been gradually exploited for raw chemical materials. A recent remarkable advance in petrochemical technology accelerates the exploitation, enabling the expectation that more proportions of petroleum will be used for chemical uses.

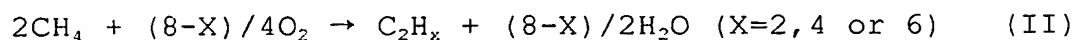
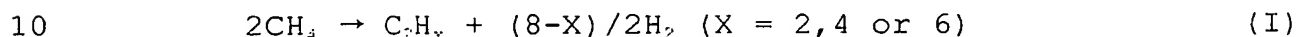
From petroleum, various organic compounds can be prepared. Of them, ethylene and propylene are well known to be very useful over a wide range of uses. Particularly, ethylene, called a flower of petrochemistry, has its uses which are too many to enumerate.

Because world oil deposits are known to be limited, in estimation, to another 30-40 year quantity, exploration for the raw materials needed to prepare ethylene and other compounds is a very interesting research subject to the artisan. Meanwhile, natural gas, which is estimated to be buried at a significant amount, has already been substituted for petroleum in many parts of the world. With a reasonable possibility, active research has been and continues to be directed to the application of natural gas as a raw chemical material.

Natural gas consists mainly of methane. The structure of this compound is thermodynamically very stable so that it is not easily broken. Nonetheless, much effort is made to activate methane, that is, to break the bond between the constituents, carbon and hydrogens, with the aim of preparing various carbohydrates therefrom. For instance, methanol, ethanol, formaldehyde, ethane, ethylene, propane and aromatic carbohydrates, which are and will be used as indispensable chemical raw materials, may be prepared by activating methane. For this reason, various studies have actively made on the

activation of methane, directed mainly to ethylene production.

In order to prepare low carbohydrates, such as ethylene, ethane, propane, etc, from methane, a coupling reaction of methane is conventionally utilized in which methane is catalytically activated by use of transition metal oxides. The coupling reaction, well known as a conversion reaction of methane, is largely divided into dehydrogenation (I) and oxidation (II) as follows:



The methane activation which has been known thus far is accomplished primarily by use of transition metal oxide catalysts. Aiming to establish high efficiency and good reaction conditions, the study on such a coupling reaction, which was started by Keller and Bhasin, is now one of the hottest issues over the world in the art. Owing to the coupling reaction, methane is recognized as a new chemical resource which is highly competitive.

However, the conventional coupling reaction has a significant problem of being effective only at a high temperature ranging from approximately 600 to 800 °C. In other words, the facility and energy invested in producing the desired products through the conventional coupling reaction

increase in cost relative to the high temperature required. In addition, the high temperatures cause the production of a large quantity of pollution, such as carbon dioxide. Further, since the products of the coupling reaction, e.g. ethane and ethylene, are more reactive to oxygen than is the reactant, methane, the activity of the reaction catalyst used is usually restricted to 10 % or so and hence, the selectivity thereof is low, as well. Consequently, the conventional method has every reason to be improved.

In current, ethylene is produced from petroleum refining fractions by a thermal cracking process, which also requires a temperature of 800 °C or higher as in the coupling reaction of methane, so that there is still a problem of high cost for the facility and energy. However, the thermal cracking process is advantageous owing to its capability of large-scale production provided that petroleum is abundant and cost-competitive.

Taking the aforementioned situations into account, many scientists and technicians the world over have made and are making much effort to convert methane into desired compounds under a preferred condition, such as room temperature and/or atmosphere, by photoreactions. A representative research work was published by Hightower, J.W. (Ed., Studies in Surface Science and Catalysis, Vol. 101, Elsevier, Amsterdam, 1996, pp 407-416), disclosing that methanol is prepared from water and

methane in the presence of a photocatalyst comprising tungsten oxide as an active ingredient. The reason why the final product is not a low carbohydrate, such as ethane, ethylene, propane, etc, but methanol, is that the methane coupling  
5 reaction driven by the photocatalyst is of very low efficiency.

### Disclosure of the Invention

10 It is, therefore, an object of the present invention to overcome the aforementioned problems and to provide a photocatalyst for converting methane, which is activated at ordinary temperature and atmospheric pressure by artificial light, such as uv light.

15 It is another object of the present invention to provide a method for preparing low carbohydrates, such as ethylene, ethane, propane, etc, from methane at low costs without causing the production of pollution of the environment.

20 The present invention, which resulted from the intensive and thorough research of the present inventors, is based on the finding that a precious metal, selected from Pd, Ir, Ru, Cd, Cu, Ag and Pt, can play a splendid role as a photocatalytically active ingredient when it is impregnated in a support, selected from ZnS, CdS and TiO<sub>2</sub>. Illumination of

artificial light upon a homogeneous suspension of the photocatalyst and methane in water can generate low carbohydrates, such as ethane, ethylene and propane, without difficulty at 5-55 °C under a pressure of a vacuum to 5 atm.

5           Accordingly, in an aspect of the present invention, there is provided a photocatalyst, represented by the following formula III:



10

wherein M stands for a metal selected from the group consisting of Pd, Ir, Ru, Cd, Ag and Pt; S stands for a support selected from the group consisting of ZnS (Zn:S 1:1 molar ratio), CdS (Cd:S 1:1 molar ratio) and TiO<sub>2</sub> (anatase type); and A represents the amount of the M impregnated, ranging from 0.50 to 3.50 weight % based on the total weight of the photocatalyst (M+A).

15

In another aspect of the present invention, there is provided a method for preparing a photocatalyst, in which a solution of a metal (M) in water is added with a support in such a way that the amount of the metal ranges from 0.50 to 3.50 weight % based on the total weight of the metal and the support, stirred for 18-30 hours at 40-70 °C, dried for 20-28 hours at 80-200 °C and sintered at 250-550 °C.

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25           In a further aspect of the present invention, there is



provided a method for preparing low carbohydrates, in which a suspension of the photocatalyst in water is added with a sufficient amount of methane with stirring, and irradiated with artificial light, such as uv light, at 5-55 °C under a pressure of a vacuum-5 atm.

### Best Modes for Carrying Out the Invention

The present invention pertains to a photocatalyst which can efficiently convert methane into low carbohydrates. The photocatalyst consists of an inorganic active ingredient and a support, in accordance with the present invention. The inorganic active ingredient is selected from the group consisting of palladium, iridium, ruthenium, cadmium, copper, argentine and platinum. As for the support, it is selected from the group consisting of zinc sulfide, cadmium sulfide and titan dioxide. In this support group, zinc sulfide and cadmium sulfide are preferably comprised of a 1:1 molar ratio of Zn:S and Cd:S, respectively. Preferable titan dioxide is an anatase type. The most preferable in the support group is titan dioxide in light of the experiment data which showed that the ZnS, CdS and TiO<sub>2</sub> photosupports have a methane conversion rate of 0.0053%, 0.0045% and 0.0120%, respectively.

The present invention also pertains to preparation of the

photocatalyst. A selected, active metal is mixed with a selected support in such a way that the metal is present at an amount of 0.50-3.50 weight % based on the total weight of the metal and the support. The resulting mixture is stirred for 18-30 hours at 40-70 °C. After being completely dried for 20-28 hours at 80-200 °C, the mixture is subjected to sintering at 250-550 °C. In regard to a sintering process, one of the following routes may be taken:

1. sintering at 450-550 °C for 1.5-2.5 hours in an electric furnace without any flow of air (partial oxidation sintering);

2. sintering at 450-550 °C for 1.5-2.5 hours with an air flow at a speed of 45-55 cc per min (complete oxidation sintering); and

3. sintering at 250-350 °C for 1.5-2.5 hours with an air flow at a speed of 45-55 cc per min and then, at 250-350 °C for 1.5-2.5 hours with a hydrogen flow at a speed of 45-55 cc per min, or sintering at 250-350 °C for 1.5-2.5 hours with an air flow at a speed of 45-55 cc per min and then, at 500 °C for 1.5-2.5 hours with a hydrogen flow at a speed of 45-55 cc per min (complete oxidation-after-reduction sintering).

Examples of the salts containing the photocatalytically active metals include  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{AgNO}_3$ ,  $\text{PdCl}_2$ ,  $\text{IrCl}_3 \cdot x\text{HCl} \cdot y\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ . The active metal M is preferably impregnated at an amount of approximately

0.50-3.50 weight % based on the total weight of the photocatalyst and most preferably at an amount of approximately 2.00 weight %.

The present invention also pertains to a photoreaction in the preparation of the photocatalyst. A suspension of the photocatalyst in water is added with a sufficient amount of methane with stirring. In a photoreactor, the resulting suspension is irradiated with artificial light, such as uv light, to produce ethane, ethylene and propane. For this photoreaction, the photoreactor is maintained at a temperature of 5-55 °C and at a pressure of a vacuum to 5 atm and preferably at room temperature and ordinary pressure.

A better understanding of the present invention may be obtained in light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention. In the following examples, the conversion rate of methane and the selectivity of products are defined as follows:

Conversion Rate of Methane =  $\frac{\text{Moles of Methane fed} - \text{Moles of Methane left after photoreaction}}{\text{Moles of Methane fed}} \times 100$

Selectivity of Product =  $\frac{\text{Moles of Product}}{\text{Moles of methane converted}} \times 100$

## PREPARATION EXAMPLES I THROUGH V

1) Pd/TiO<sub>2</sub> (anatase type) Catalyst

To 6.093 g of completely dried TiO<sub>2</sub> (anatase type) was added a suspension of 0.203 g of PdCl<sub>3</sub> in 60 cc of water. The resulting suspension was stirred for 24 hours at 50-60 °C while removing water, dried for 24 hours at 110 °C, and divided among the three, each of which was subjected to the following sintering processes to give three photocatalysts:

A. sintering at 500 °C for 2.0 hours in an electric furnace without any air flow.

B. sintering at 500 °C for 2.0 hours in an electric furnace with an air flow of 50 sccm.

C. sintering at 300 °C for 2.0 hours in an electric furnace with an air flow of 50 sccm, followed by reduction sintering at 300 °C for 2.0 hours with a hydrogen flow of 50 sccm.

2) Pt/TiO<sub>2</sub>(anatase type) Catalyst

The title catalyst was prepared in a similar manner to that of Preparation Example I, except that a solution of 0.256 g of platinum chloride (H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O) in 60 cc of water was added to 6.093 g of completely dried titan dioxide (anatase type).

3) Ir/TiO<sub>2</sub>(anatase type) Catalyst

The title catalyst was prepared in a similar manner to that of Preparation Example I, except that a solution of 0.095 g of iridium chloride (IrCl<sub>3</sub>·xHCl·yH<sub>2</sub>O) in 60 cc of water was added to 3.047 g of completely dried titan dioxide (anatase type).

4) Ru/TiO<sub>2</sub>(anatase type) Catalyst

The title catalyst was prepared in a similar manner to that of Preparation Example I, except that a solution of 0.095 g of ruthenium chloride (RuCl<sub>3</sub>·xHCl) in 60 cc of water was added to 3.047 g of completely dried titan dioxide (anatase type).

5) Ir/TiO<sub>2</sub>(anatase type) Catalyst

The title catalyst was prepared in a similar manner to that of Preparation Example I, except that a solution of 0.248 g of cadmium chloride (CdCl<sub>2</sub>·2.5HCl) in 60 cc of water was added to 6.093 g of completely dried titan dioxide (anatase type).

## PREPARATION EXAMPLES VI AND VII

6) Cu/TiO<sub>2</sub>(anatase type) Catalyst

To 3.047 g of completely dried TiO<sub>2</sub> was added a solution

of 0.164 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 60 cc of water. This resulting solution was stirred for 24 hours at 50-60 °C while removing water, dried for 24 hours at 110 °C and then, divided among the three. The title photocatalysts were prepared by sintering the trisected materials in the same manners as those of Preparation Examples I through V.

7)  $\text{Ag}/\text{TiO}_2$  (anatase type) Catalyst

The title catalyst was prepared in a similar manner to that of Preparation Example I, except that a solution of 0.096 g of cadmium chloride ( $\text{AgNO}_3$ ) in 60 cc of water was added to 3.047 g of completely dried titan dioxide (anatase type).

EXAMPLES I THROUGH VII : Activation of Methane by Partially Oxidized Catalyst

An artificial uv light source was installed in a reactor 500 cc in volume of a photoreaction system 805 cc in volume, to distribute the light sufficiently and uniformly in the reactor while heat was insulated by cooling water. In the reactor which could circulate its internal air, 500 cc of purified water and 1 g of each of the partially oxidized palladium, platinum, iridium, ruthenium, cadmium, copper and silver catalysts which were prepared via the sintering process A of Preparation Example I, were charged. The atmosphere of

the reaction system was substituted with methane by feeding for 30 min. Then, the air current inside the photoreaction system was isolated from the exterior and uv light was radiated at 25 °C under an ordinary pressure. At one hour after the uv irradiation, the products of the above photoreaction were quantitatively analyzed via gas chromatography (1/8 x 6'/st.st., chromosoph 102, FID, N<sub>2</sub>). The compositions of the products were found to be dependent on the synthesized catalysts, and are given in Table I, below.

#### COMPARATIVE EXAMPLE I : Activation of Methane by Partially Oxidized Catalyst

A Rh/TiO<sub>2</sub> photocatalyst was prepared in a similar manner to the sintering process A of Preparation Example I (partial oxidation at 500 °C without any air flow), except for using a solution of 0.248 g of rhodium chloride (RhCl<sub>3</sub>·xH<sub>2</sub>O), instead of palladium chloride, in 60 cc of water. Using 1 g of this partially oxidized photocatalyst, the procedure of Example I was repeated to produce products. The composition of the products is given in Table 1, below.

Table 1  
Products Converted from Methane by Partially Oxidized Catalysts

Nos. of Exmp.	Catalyst (Metal/TiO <sub>2</sub> )	Me. <sup>1</sup> Conv. Rate(%)	Composition (%)			Selectivity			Ethy. /Et.
			Ethy. <sup>2</sup>	Et. <sup>3</sup>	Pro. <sup>3</sup>	Ethy.	Et.	Pro.	
I	Pd	0.982	7.3x10 <sup>-4</sup>	2.5x10 <sup>-2</sup>	3.3x10 <sup>-3</sup>	1.2	40.3	5.3	0.030
II	Pt	0.697	3.5x10 <sup>-4</sup>	1.0x10 <sup>-3</sup>	2.2x10 <sup>-3</sup>	0.8	41.9	5.1	0.019
III	Ir	0.224	1.5x10 <sup>-4</sup>	6.9x10 <sup>-3</sup>	6.8x10 <sup>-4</sup>	1.1	49.3	4.9	0.022
IV	Ru	0.168	2.7x10 <sup>-4</sup>	5.4x10 <sup>-3</sup>	2.9x10 <sup>-4</sup>	2.5	49.1	2.6	0.051
V	Cd	0.295	9.3x10 <sup>-2</sup>	8.6x10 <sup>-4</sup>	5.6x10 <sup>-4</sup>	0.5	45.3	2.9	0.011
VI	Cu	0.200	6.0x10 <sup>-4</sup>	5.7x10 <sup>-3</sup>	3.4x10 <sup>-4</sup>	5.0	47.5	2.8	0.105
VII	Ag	0.200	4.0x10 <sup>-4</sup>	6.3x10 <sup>-3</sup>	4.1x10 <sup>-4</sup>	3.1	40.8	3.2	0.075
C.I	Rh	trace <sup>5</sup>	trace <sup>6</sup>	trace <sup>6</sup>	trace <sup>6</sup>	-	-	-	-

<sup>1</sup> Methane Conversion Rate

<sup>2</sup> Ethylene, <sup>3</sup> Ethane, <sup>4</sup> Propane

<sup>5</sup> < 0.100, <sup>6</sup> < 1.0x10<sup>-4</sup>

EXAMPLES VIII THROUGH XI : Activation of Methane by Completely Oxidized Catalyst

The same procedures as those of Examples I-VII were repeated, except that 1 g of each of the palladium, platinum, copper and silver catalysts which were prepared via the sintering process B of Preparation Example I (oxidation at 500 °C with an air flow at 50 sccm), to produce products whose compositions are given in Table 2, below.

COMPARATIVE EXAMPLE II : Activation of Methane by Completely



## Oxidized Cobalt Catalyst

A cobalt photocatalyst was prepared in a similar manner to the sintering process B of Preparation Example I (oxidation at 500 °C with an air flow at 50 sccm), except for using a solution of 0.603 g of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), instead of palladium chloride, in 60 cc of water. Using 1 g of this completely oxidized cobalt catalyst, the procedure of Example I was repeated to produce products whose composition is given in Table 2, below.

Table 2  
Products Converted from Methane by Completely Oxidized Catalysts

Nos. of Exmp.	Catalyst (Metal/ $\text{TiO}_2$ )	Me. <sup>1</sup> Conv. Rate(%)	Composition (%)			Selectivity (%)			Ethy. /Et.
			Ethy. <sup>2</sup>	Et. <sup>3</sup>	Pro. <sup>3</sup>	Ethy.	Et.	Pro.	
VIII	Pd	1.312	$1.4 \times 10^{-3}$	$3.3 \times 10^{-2}$	$3.9 \times 10^{-3}$	1.7	40.2	4.8	0.042
IX	Pt	1.440	$4.0 \times 10^{-4}$	$3.1 \times 10^{-2}$	$6.1 \times 10^{-3}$	0.4	34.4	5.8	0.012
	Ir	-	-	-	-	-	-	-	-
	Ru	-	-	-	-	-	-	-	-
	Cd	-	-	-	-	-	-	-	-
X	Cu	0.480	$4.3 \times 10^{-4}$	$1.2 \times 10^{-2}$	$1.3 \times 10^{-3}$	1.4	40.0	4.3	0.035
XI	Ag	0.208	$2.2 \times 10^{-4}$	$5.4 \times 10^{-3}$	$6.4 \times 10^{-4}$	1.7	41.5	4.9	0.041
C.II	Co	trace <sup>5</sup>	trace <sup>6</sup>	trace <sup>6</sup>	trace <sup>6</sup>	-	-	-	-

<sup>1</sup> Methane Conversion Rate

<sup>2</sup> Ethylene, <sup>3</sup> Ethane, <sup>4</sup> Propane

<sup>5</sup> < 0.100, <sup>6</sup> <  $1.0 \times 10^{-4}$

EXAMPLES XII THROUGH XVI : Activation of Methane by Completely

## Reduced Catalyst

The same procedures as those of Examples I-VII were repeated, except that 1 g of each of the palladium, platinum, iridium, ruthenium and cadmium catalysts which were prepared via the sintering process C of Preparation Example I (sintering at 300 °C with an air flow at 50 sccm, followed by reducing at 300 °C with a hydrogen flow at 50 sccm), to produce products whose compositions are given in Table 3, below.

## EXAMPLE III : Activation of Methane by Completely Reduced Zinc Catalyst

A zinc catalyst was prepared in a similar manner to the sintering process C of Preparation Example I (sintering at 300 °C with an air flow at 50 sccm, followed by reducing at 300 °C with a hydrogen flow of 50 sccm), except for using a solution of 0.555 g of zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), instead of palladium chloride, in 60 cc of water. Using 1 g of this completely reduced zinc catalyst, the procedure of Example I was repeated to produce products whose composition is given in Table 3, below.

## EXAMPLES XVII AND XVIII : Activation of Methane by Completely

## Reduced Copper and Silver Catalysts

The same procedures as those of Examples I-VII were repeated, except that 1 g of each of the copper and silver catalysts which were prepared via the sintering process C of Preparation Example I (sintering at 300 °C with an air flow at 50 sccm, followed by reducing at 300 °C with a hydrogen flow at 50 sccm), to produce products whose compositions are given in Table 3, below.

## COMPARATIVE EXAMPLE IV : Activation of Methane by Completely Reduced Iron Catalyst

An iron catalyst was prepared in a similar manner to the sintering process C of Preparation Example I (sintering at 300 °C with an air flow at 50 sccm, followed by reducing at 300 °C with a hydrogen flow of 50 sccm), except for using a solution of 0.883 g of ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), instead of palladium chloride, in 60 cc of water. Using 1 g of this completely reduced zinc catalyst, the procedure of Example I was repeated to produce products whose composition is given in Table 3, below.

Table 3  
Products Converted from Methane by Completely Reduced Catalysts

Nos. of Exmp.	Catalyst (Metal/ TiO <sub>2</sub> )	Me. <sup>1</sup> Conv. Rate(%)	Composition (%)			Selectivity			Ethy. /Et.
			Ethy. <sup>2</sup>	Et. <sup>3</sup>	Pro. <sup>3</sup>	Ethy.	Et.	Pro.	
XII	Pd	1.088	1.9x10 <sup>-4</sup>	3.0x10 <sup>-3</sup>	3.2x10 <sup>-3</sup>	0.3	44.1	4.7	0.010
XIII	Pt	0.688	2.7x10 <sup>-4</sup>	1.6x10 <sup>-4</sup>	2.1x10 <sup>-3</sup>	0.6	41.9	4.0	0.014
XIV	Ir	0.016	7.1x10 <sup>-5</sup>	5.4x10 <sup>-4</sup>	1.0x10 <sup>-4</sup>	7.1	54.0	10.0	0.131
XV	Ru	0.432	1.8x10 <sup>-4</sup>	1.2x10 <sup>-3</sup>	1.0x10 <sup>-4</sup>	0.7	44.4	3.7	0.015
XVI	Cd	0.048	6.8x10 <sup>-6</sup>	1.4x10 <sup>-3</sup>	4.2x10 <sup>-5</sup>	2.3	46.7	1.4	0.049
XVII	Cu	0.448	4.4x10 <sup>-4</sup>	1.2x10 <sup>-2</sup>	1.3x10 <sup>-3</sup>	1.6	42.9	4.6	0.037
XVIII	Ag	0.240	2.5x10 <sup>-4</sup>	6.7x10 <sup>-3</sup>	4.9x10 <sup>-4</sup>	1.7	44.7	3.3	0.038
C.III	Zn	trace <sup>5</sup>	trace <sup>6</sup>	trace <sup>6</sup>	trace <sup>6</sup>	-	-	-	-
C.IV	Fe	trace <sup>5</sup>	trace <sup>6</sup>	trace <sup>6</sup>	trace <sup>6</sup>	-	-	-	-

<sup>1</sup> Methane Conversion Rate<sup>2</sup> Ethylene, <sup>3</sup> Ethane, <sup>4</sup> Propane<sup>5</sup> < 0.100, <sup>6</sup> < 1.0x10<sup>-4</sup>

### Industrial Applicability

As apparent from the examples, while showing stability as reaction catalysts, the photocatalysts according to the present invention have an ability to photo-activate methane at efficiencies which had been not yet accomplished by conventional catalysts. Consequently, in the presence of the photocatalysts, methane can be converted into low carbohydrates, such as ethylene, ethane and propane, at low costs without causing the production of pollution of the

environment.

The present invention has been described in an illustrative manner, and it is to be understood the terminology used is intended to be in the nature of  
5 description rather than of limitation. Many modifications and variations of the present invention are possible in light of the above teachings. Therefore, it is to be understood that within the scope of the appended claims, the invention may be  
10 practiced otherwise than as specifically described.

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**Claims**

1. A photocatalyst for converting methane, comprising a composition represented by the following formula III:



wherein M stands for a metal selected from the group consisting of Pd, Ir, Ru, Cd, Ag and Pt; S stands for a support selected from the group consisting of ZnS (Zn:S 1:1 molar ratio), CdS (Cd:S 1:1 molar ratio) and  $TiO_2$ ; and A represents the amount of the M impregnated, ranging from 0.50 to 3.50 weight % based on the total weight of the photocatalyst (M+A).

2. A photocatalyst as set forth in claim 1, wherein said  $TiO_2$  is an anatase type.

3. A method for preparing a photocatalyst for use in converting methane, in which a metal salt which comprise a catalytically active metal selected from the group consisting of Pd, Ir, Ru, Cd, Cu, Ag and Pt, is dissolved in water and mixed with a dried support selected from the group consisting of ZnS, CdS and  $TiO_2$ , in such a way that the metal is present

at an amount of 0.50-3.50 weight % based on the total weight of the metal and the support, and the resulting mixture is stirred for 18-30 hours at 40-70 °C, completely dried for 20-28 hours at 80-200 °C, and subjected to a sintering process at  
5 250-550 °C.

4. A method as set forth in claim 3, wherein said sintering process is a partial oxidation sintering process, a complete oxidation sintering process, or a complete oxidation-  
10 after-reduction sintering process.

5. A method as set forth in claim 4, wherein said partial oxidation sintering process is carried out at 450-550 °C for 1.5-2.5 hours without any flow of air.

6. A method as set forth in claim 4, wherein said complete oxidation sintering process is carried out at 450-550 °C for 1.5-2.5 hours with an air flow at a speed of 45-55 cc per min.

7. A method as set forth in claim 4, wherein said complete oxidation-after-reduction sintering process is carried out at 250-350 °C for 1.5-2.5 hours with an air flow at a speed of 45-55 cc per min and then, at 250-550 °C for  
20 1.5-2.5 hours with a hydrogen flow at a speed of 45-55 cc per  
25

min.

8. A method as set forth in claim 3, wherein said metal salt is selected from the group consisting of  $\text{PdCl}_2$ ,  
5  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ ,  $\text{IrCl}_3 \cdot x\text{HCl} \cdot y\text{H}_2\text{O}$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ,  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  
and  $\text{AgNO}_3$ .

9. A method for preparing low carbohydrates, in which a suspension of the photocatalyst of claim 1 in water is added  
10 with a sufficient amount of methane with stirring, and  
irradiated with artificial light.

10. A method as set forth in claim 9, wherein the photoreaction is carried out at 5-55 °C under a pressure of a  
15 vacuum-5 atm.



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR 98/00224

## A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>6</sup>: B 01 J 23/38,23/06,27/04,37/12,37/16; C 07 C 2/84

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>6</sup>: B 01 J; C 07 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	CN 1 120 469 (UNIV.HUANAN SCI & ENG) 17 April 1996 (17.04.96), (abstract) [online] [retrieved on 15.04.99] retrieved from: EPO WPI database.	1-10
A	EP 0 486 951 A2 (HUGHES AIRCRAFT COMPANY) 27 May 1992 (27.05.92), examples; claims.	1,3,9
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☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

„O“ document referring to an oral disclosure, use, exhibition or other means

„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&“ document member of the same patent family

Date of the actual completion of the international search

26 April 1999 (26.04.99)

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 98/00224

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